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SELECTIVITY IN ZEOLITE OCCLUSION OF OLEFINS

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Selectivity in Zeolite Occlusion of Olefins

Selective occlusions of straight-chain paraffins in the presence of branched-chain hydrocarbons by naturally occurring zeolites of suitable dimension was reported as early as 1944 by Barrer and Ibbitson.[1] More recently the capacity of synthetic zeolites or molecular sieves to absorb exclusively the straight-chain hydrocarbons from complex hydrocarbon mixtures has found extensive application in the petroleum industry. Under the conditions developed for most sieving operations[2] any normal olefins present are occluded along with the normal paraffins. A supplemental separation technique must be employed to obtain n-paraffins free of olefins.[3]

Molecular sieving has become important in this laboratory in the separation and analysis of organic material extracted from ancient geological strata.[4] It is the method used to separate and recover long straight chain hydrocarbons from a "total hydrocarbon" extract containing straight and branched chain paraffins and olefins and clicyclic hydrocarbons. Vapor phase chromatography (VPC) of the non-occluded hydrocarbon mixtures recovered from the supernatants in sieving operations on different rock extracts suggested that normal olefins were present with the non-occluded branched hydrocarbons in addition to being occluded with the normal hydrocarbons.[4] Considered in view of the nearly unanimous literature assertion[2,3,5] that it is impossible to occlude paraffins without also occluding all normal olefins present, this observation seemed important to investigate.

Octadecene-1, cis-octadecene-9 and trans-octadecene-9 were chosen as representatives of n-olefins in the weight range of the compounds of geochemical interest. n-Octadecane was obtained from Eastman and judged at least 98% pure from its mass spectrum, infrared spectrum, nuclear magnetic resonance spectrum and vapor phase chromatogram. 1-Octadecene was purchased from Matheson, Coleman

and Bell and was similarly characterized as better than 95% chemically pure by the four methods listed above. Isomeric contamination was less than 5%. Trans-9-octadecene was synthesised from elaidic acid (K and K Laboratories). Elaidic acid was reduced to trans-9-octadenol-1 with lithium aluminum hydride. The tosylate of the resulting alcohol was prepared and reduced with lithium aluminum hydride. The product, trans-9-octadecene, was purified by chromatography in hexane on a short alumina column. The trans olefin was characterized as greater than 95% chemically pure. Cis- and trans-9-octadecene could be separated by thin layer chromatography on silver nitrate-impregnated silica gel. The amount of contamination of trans-9-octadecene by the cis isomer was determined to be about 1% by recovering the bands from preparative thin layer chromatoplates and analyzing them by VPC. No chexk was made for position isomers. Cis-9-octadecene was synthesized from oleic alcohol [12] from K and K Laboratories which itself contained considerable amounts of the trans isomer. Consequently the synthetic cis olefin (95% chemically pure) contained 12-15% trans material.

Linde sieves (5Å) were employed in the form of 1/16 inch pellets. These were dried for at least 18 hr. at 350° at atmospheric pressure before use. In each experiment the four C_{18} hydrocarbons were sieved separately with sieves from the same batch and solvent from the same bottle. Octadecane (200 mg.), octadecene (200 µl.), cis-9-octadecene (200 µl.) and trans-9-octadecene (200 µl.) were each combined with 8.0 g. 5Å sieves in 50 ml. of benzene or cyclohexane. The benzene used was redistilled reagent grade and the cyclohexane was chromatography grade which had been stored over molecular sieves. The sieving mixtures were heated under reflux for 1 to 3 days until vapor phase chromatograms of the supernatant from the octadecane flask indicated that no more of the saturated material was being occluded.

When the experiment was stopped, the supernatant was decanted and the sieves were transferred to Soxhlet extractors where they were washed with fresh

solvent (benzene or cyclohexane) for 5-6 hr. This wash, which always contained very little C_{18}-hydrocarbon, was combined with the supernatant and the solvent was evaporated. The recovered non-occluded material was transferred to a volumetric flask which was filled to volume with benzene. The sieves were dissolved with magnetic stirring in ice-cooled 24% hydrofluoric acid under a layer of benzene. The acidic solution was separated from the benzene layer and was washed twice with benzene. The combined benzene fractions were washed with bicarbonate solution and water and were dried over magnesium sulfate. After filtration the benzene was evaporated and the residue was transferred to a volumetric flask. The volumetric solutions of occluded and non-occluded material were compared by vapor phase chromatography with similar solutions of known concentration. For this work a 10 ft. SE-30 column was used. Vapor phase and thin layer chromatograms and infrared spectra of the recovered materials were obtained. The distribution of each hydrocarbon between sieve and supernatant is presented in Table I. From these data several conclusions can be drawn: The presently reported experiments demonstrate that under the solution conditions used, with occlusion of normal octadecane to equilibrium functioning as the standard time, various isomers of n-octadecene are occluded to quite different extents. A second conclusion is that a significant solvent effect is revealed by the increase in the amounts of cis-9-octadecane and 1-octadecene occluded in cyclohexane relative to benzene. Also attesting to the solvent effect is the much shorter period (one-half to two-thirds as long) required to complete sieving of the reference alkane in cyclohexane. Temperature is not a variable here since the two solvents boil within 1.5°C of each other. A third conclusion is that little or no isomerization or polymerization occurs in the material which is exposed to the sieves but is not occluded by them. Polymerization is excluded by the mass balance obtained in the recovered materials identified by vapor phase chromatography. Isomerization of the non-occluded cis and terminated olefins is excluded by

infrared measurements[12] of material recovered from the supernatant. Cis and terminal olefins recovered by hydrofluoric acid solution of the sieves had isomerized to a considerable extent. Isomerization apparently occured in or on the sieves, since 1-octadecane which was stirred with 8 g. unused sieves in 24% hydrofluoric acid in a blank run was recovered with little or no isomerization.

Table I

Distribution of hydrocarbon between sieve and supernatant

	n-Octadecane (mg.)			1-Octadecene (µl.)			trans-9-Octadecene (µl.)		cis-9-Octadecene (µl.)	
Trial	1	2	3	1	2	3	1	2	1	2
Occluded from Benzene	200	200	200	18	5	1	200	200	15	4
Benzene Supernatant	4	<1	<1	184	200	200	7	5	186	200
Trial	4	5		4	5		4	5	4	5
Occluded from Cyclohexane	200	200		40	40		190	200	170	195
Cyclohexane Supernatant	<1	<1		150	160		<1	<1	25	5

Each pair of sieve and supernatant numbers represents a separate sieving experiment.

In the literature report most pertinent to the long-chain olefins considered here, O'Conner and Norris found that 1-hexene, trans-3-hexene, cis-3-hexene and 1-hexadecene are all occluded in less than 2.5 hr. when applied to a column of molecular sieves as neat solutions. According to these results, none of the

three kinds of normal olefins-- cis, trans, terminal-- is sterically excluded from the sieves. All three olefins are small enough to pass through the orifice (approximately 5Å).

The major difference between the present work and that of most other investigators is the use of a dilute (0.4%) solution[8] (instead of gaseous or neat liquid applications) to bring the normal hydrocarbons into contact with the sieves. There are two schools of thought concerning the sieving of a sorbable compound from a non-sorbable solvent. One group of workers[9] reports that the adsorption isotherm for the sorbable compound is independent for the solvent. Another view presented recently by Jain, Gerhardt and Ryle,[10] states that "liquid phase adsorption equilibria strongly depend on liquid phase solution behavior." These authors submit evidence supporting a phase partition equilibrium, which is definitely affected by the nature of the non-occludable solvent. The data in Table I certainly indicate a solvent effect for dilute solutions.

If the results on the olefins can be considered to approximate equilibrium values, the spectacular solvent effect on the occlusion of cis-9-octadecene would seem to require some additional consideration which might indeed cover the entire pattern presented in the table. If the presumption is made that some kind of molecular interaction between benzene and the exposed double bonds of the cis compound and the terminal olefin is involved which reduces the chemical potential of these olefins in dilution solution and which cannot operate when the olefins are in the sieve, one can account at least qualitatively for the results shown in the table, for both cis-9-octadecene and 1-octadecene. The fact that the trans-9-octadecene is occluded from both solvents would speak for the lack of any significant interaction between the double bond in this compound and the solvent, whether it be by benzene or cyclohexane.

On the other hand, the selectivity observed may reflect a kinetic phenomenon. It has been suggested[9b] that the more strongly a compound is adsorbed in the sieve

the slower is its approach to occlusion equilibrium. Following this line of reasoning one might suggest that terminal and cis olefins are more strongly attracted and held by the polar sites in the sieves, perhaps because the double bonds are more exposed, and are thus more slowly occluded than the trans olefin. If this kinetic explanation is accepted, it must then be brought into agreement with the observed solvent effect. Clearly a kinetic investigation is required here as well as further thermodynamic determinations on the solvents themselves.

With respect to the original problem, it has been ascertained that under the conditions[4] used to sieve the geochemical samples only the normal trans olefins can be assumed to be occluded with the normal alkanes. Most probably normal terminal olefins and cis olefins will remain in the benzene supernatant.

If a mixture of a wide range of homologous hydrocarbons (e.g. C_{12}-C_{36}) is sieved under conditions sufficient to occlude the normal saturated hydrocarbons of higher molecular weights, it may be that more of the normal cis and terminal olefins of lower molecular weights will be occluded (along with the trans olefins) in spite of their slower rate. Thus different amounts of olefins might be occluded from different geochemical mixtures. If the complete separation of olefins from a homologous mixture of parafins is desired, chromatography (especially thin-layer) on an adsorbant impregnated with silver nitrate is recommended.

A possible application of measurements such as these to help in the understanding of the penetration of hydrocarbons through lipid membranes in biological systems is only just begining. We are exploring this aspect more extensively and will report on it later.

[1]Barrer, R. M., and Ibbitson, D. A., Trans. Farad. Soc., 40, 195 (1944).

[2]For examples see (a) Holt, R. L., and Crawley, C. L., U.S. Patent 3, 150, 202, Sept. 22, 1964. (b) O'Connor, J. G., and Norris, M. S., Anal. Chem. , 32, 701 (1960). (c) Nelson, K. H., Grimes, M. D., and Heinrich, B. J., Anal. Chem. 29, 1026 (1957). (d) Brenner, N., Cieplinski,E., Ettre, L. S., and Coates, V. J., J. Chromatography, 3, 230 (1960). (e) Kasperik, A. S., and Justus, S. C., U.S. Patent 2, 963, 519, Dec. 6, 1960. (f) Hawes, T. P., U.S. Patent 3, 146, Aug. 25, 1964. (g) Duffett, R. H. E., and Minkoff, G. J., Discovery, December, 1964, p. 32. (h) Dantos, S., Chem. Eng. , 71, no. 25, 155, (1964)..

[3] (a) Schwartz, R. D., and Brasseaux, D. J., Anal. Chem., 29, 1022(1957). (b) Nelson, K. H., Grimes, M. D., and Heinrich, B. J., Anal.Chem.,29, 1026 (1957). (c) Kimberlin, Jr., N., and Mattox, W. J., U.S. Patent 2,971,993, Feb. 14, 1961.

[4]Eglinton, G., Scott, P. M., Belsky, T., Burlingame, A. L., Richter, W., and Calvin, M., in Advances in Organic Geochemistry 1964, International Series of Monographs in Earth Sciences, Volume 24, Edited by G. D. Hobson and M. C. Louis, Pergamon Press, Oxford, 1966.

[5]The abstracts of several papers in Russian do suggest that cis olefins are not occluded as readily as other olefins in the gas phase. (a) Kvitkivskii, L. N., Kramskois, V. P., and Gutyrya, V. S., Neftekhimiya, 3, 882 (1963) C. A. 60, 5255g. (b) Vinogradova, V. S., Efimova, G. I., Kofman, L. S., and Lukashina, V. M. Razdelenie i S Analiz Uglevodorodynkh Gazov, Adad. Nauk SSSR, Inst. Neftekhim, Sinteza, Sb.Statei 54 (1963) C. A. 60 15658a.

[6]Selective recovery has been reported by Shell International Research Maatschapp, British Patent 890,555, March 7, 1962.

[7]Gelb, L. L., Port, W. S., and Ault, W. C., J. Org. Chem. 23, 2022 (1958).

[8]The dilute solution (< 5%) technique has been previously employed, although apparently not for olefins. For example see (a) Boroughs, R. M., Dean, R. A., Girdler, R. B., British Patent 905, 317, Sept. 5, 1962. (b) O'Connor, J. G., Burow, F. H., and Norris, M. S., Anal. Chem., 34, 82 (1962).

[9](a) Kipling, J. J., and Wright, E. H. M., Trans. Farad. Soc., 55, 1185 (1959). (b) Private communication from Neddenriep, R. J.,,Union Carbide Corporation, Lind Division, Tonawanda, New York.

[10]Jain, L. K., Gehrhardt, H. M. and Kyle, B. G., J. Chem. and Eng. Data. 10, 202 (1965)..

[11]Isomerization and polymerization of olefins over molecular sieves are common in the gas phase. See for example (a) Norton, C. J., Chem. and Ind., (London) 258 (1962). (b) Norton, C. J., Am. Chem. Soc., Div. Petrol. Chem., Preprints 7, 195 (1962). (c) Benesi, H. A. and Peterson, D. L., U.S. Patent 3,106,593, Oct. 8, 1963. (d) Oldhan, W. J., British Patent 886,716, Oct. 21, 1959. (e) Fleck, R, N., and Wight, C. G., U.S. Patent 2,988,578, Sept 28, 1956.

[12]Dyer, M. E., Hamann, H. C., and Swern, D. S., J. Amer. Oil Chem. Soc., 43, 431 (1966), and references therein.